Norman F.H. Bancroft

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DETERMINATION OF REFRACTIVE INDEX BY THE BREWSTER ANGLE METHOD

by

J. D. Butterill

Mineralogy Section

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INTRODUCTION

On his appointment to a summer position at the Mines Branch, the writer was assigned to the Mineralogy Section of the Mineral Sciences Division, where he was given the task of developing a convenient method for measuring the refractive index of minerals by the Brewster angle method, using equipment on hand at the time. The work embodied by this report was done in the period from May 17 to August 26, 1965. The investigation was carried out under the general direction of S. A. Forman.

THEORY

When a beam of light is reflected, it becomes partially polarized, the degree of polarization depending on the angle of incidence. According to theory, the intensity of the reflected beam in the plane normal to the reflecting surface, is given by:

$$R_{\perp} = \frac{\tan^2(\theta i - \theta t)}{\tan^2(\theta i + \theta t)}$$

where θi is the angle of incidence
θt is the angle of refraction.

*Student assistant, Mineralogy Section, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa.

It can be seen that, if $(\theta i + \theta t) = \pi/2$, then $\tan^2 (\theta i + \theta t)$ becomes infinite, and $R_\perp = 0$. The angle of incidence, θi, is then known as Brewster's angle.

Since $\sin\theta i = n \sin \theta t$, where n is the index of refraction, one can find that, for Brewster's angle,

$$\sin \theta i = n \sin \theta t$$

$$= n \sin (\pi/2 - \theta i)$$

$$= n \cos \theta i$$

$$\text{or } n = \frac{\sin \theta i}{\cos \theta i} = \tan \theta i = \tan \beta$$

where $\theta i = \beta$ is Brewster's angle.

APPARATUS

The basic idea behind the apparatus used is that a beam of light should be reflected from the polished surface, whose refractive index is to be determined, through a Polaroid aligned in a plane perpendicular to the reflecting surface, and into a suitable device for measuring the resulting light intensity. The angle at which the light intensity is at a minimum (Brewster's angle) must also be measured.

Since the index of refraction of a material varies with wave length, the source of light should be monochromatic. The light also has to be collimated, since the curve of intensity versus angle of incidence is skew.

In order to arrive at the most meaningful and accurate results, a considerable time was spent initially in developing the experimental apparatus.

The samples had been mounted in bakelite rings and polished to a mirror-like surface by technicians in the Mineralogy Section, using normal polishing techniques. Since this kind of sample is not suitable for mounting directly on a goniometer head, a hole was drilled through the polished section and a length of brass rod suitable for mounting on the goniometer head was attached as shown in Figure 1.

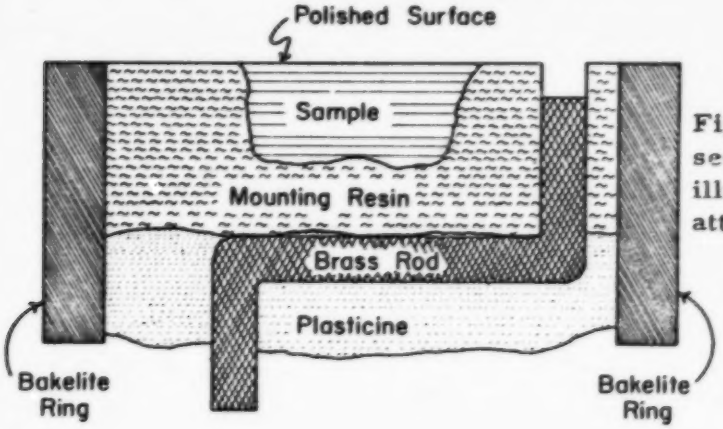

Figure 1 - Idealized cross-section of a polished section illustrating the mode of attachment of the brass rod.

A number of different light sources was tried, including a sodium vapour lamp, a 1200-W General Electric D. H. T. projection lamp, a General Electric D. M. S. bulb in a Spencer Lens Company projector, model 694, a General Electric 500-W projection bulb in a Bausch and Lomb housing, a 6-volt, 18-amp battery-powered light, and a laser of wavelength 6328 Å. Of these, the 500-W projection bulb in a Bausch and Lomb housing was found to deliver the greatest light intensity and was used throughout the experiments. It has a colour temperature of 3200° K. Because the bulb was encased in a housing designed for 100 watts, a fan was needed for cooling. The six filaments of the bulb were aligned almost parallel to the emitted beam in order to concentrate as much light as possible into a small area.

The lamp was mounted on a retort stand instead of its regular base to facilitate adjusting its position when hot. The current for the light source was provided by a voltage stabilizer made by the R. H. Nichols Company (serial No. 1355-998).

A suitable signal (a slit) had to be received from the light source so that angles could be measured accurately. (In practice, angles were measured to the nearest minute). The apparatus had to be enclosed as much as possible so that the measurements of the intensity of the signal would not include a factor due to background light, which would reduce the effect of reflective polarizing. Finally, as many stabilizing devices as practical had to be introduced to ensure comparable measurements from one moment to the next.

The light from the lamp was passed through a Bausch and Lomb diffraction grating monochromator (serial No. RD-107). The relative positions of the lamp and the monochromator had to be accurately adjusted in all dimensions to make most efficient use of the light from the lamp. The standard lenses on the input and output apertures of the monochromator were removed, in the first case to increase the intensity of the light (the lamp housing had its own lens) and, in the second case, to minimize the effect of vibration between the monochromator and the collimator. The monochromator was calibrated at a wavelength of 6328 Å using a laser beam. Both apertures on the monochromator had adjustable vertical slits, that of the output aperture constituting the slit for the signal.

The heart of the apparatus was an old two-circle goniometer manufactured by Laboratory Associates Inc. The sample was mounted on a standard adjustable goniometer head so that the polished surface was at the centre of rotation of the instrument. The light from the monochromator passed directly into the goniometer collimator (from which the normal slit and light source had been removed). The collimator was roughly perpendicular to the side of the monochromator, the position at which light was most intense. The collimated light was blacked out except for a pinhole about 3/4 mm in diameter. This beam of light was reflected from the polished surface of the sample into the goniometer telescope on which a Polaroid film had been mounted directly in front of the first lens (the collar holding the lens in place also held the Polaroid film directly against the lens). The Polaroid film was oriented to pass only light vibrating in the horizontal plane, i.e. in the plane normal to the sample surface.

The original goniometer was modified by interchanging the telescope and the goniometer arm so that the telescope could be used to measure the angle of deviation of the reflected beam directly. The scale for measuring the angle of deviation was equipped with vernier, and measurements accurate to one minute could be made. The telescope was focused at infinity, by viewing a distant object through it, and the collimator was focused so as to produce a sharp image. The top of the goniometer was covered by an enclosure that excluded almost all background light when Brewster's angle was being measured.

Initially, a cadium sulphide photo-cell was used as the light-measuring device but it was found to respond very slowly at low light intensities and to be extremely sensitive to overexposure. The photosensitive device that proved to be satisfactory was an RCA photomultiplier tube, type 1P28, enclosed in an aluminum box with a sleeve that fitted over two collars on the telescope. This allowed measurement of the light coming through the telescope. The voltage supply for the photomultiplier tube was plugged into the voltage stabilizer used for the light source.

The signal current from the photomultiplier tube, a current of up to 10^{-8} amps (ground wire was positive), was measured by a suitable millimicroammeter (Dynatron Electronics Co., model 1811). Both the voltage supply cable and the signal current cable for the photomultiplier tube were shielded. Dark current was about 10^{-10} amps.

A small shielded battery-powered light was used in measuring the angle of deviation so that the photomultiplier tube did not have to be capped in order to take a reading. This allowed light of a relatively constant intensity to fall continuously on the photomultiplier tube, further increasing stability.

OPERATING INSTRUCTIONS

The basic principle of the method that follows is that a series of light intensity readings are taken for various angles of incidence; the results are plotted and from these the minimum point on the graph, which gives Brewster's angle, is located. The step-by-step procedure is as follows:

1. Withdraw the photomultiplier tube from the telescope and cap it carefully to exclude all light. (A plug-like device was made to fit over the end of the sleeve of the aluminum casing to shut out all light).

2. Turn on the voltage stabilizer fan, voltage supply (be sure high tension is off), light source, and millimicroammeter. This is to allow all the equipment as much time as possible to warm up.

3. Set the output slit of the monochromator to 0.15 mm, and set the desired wavelength on the monochromator.

4. Be sure that the surface of the sample to be used is clean. Mount the sample on the goniometer head, keeping the sample as far as possible from the end of the pinhole device on the goniometer collimator. This is to allow sufficient room for the sample to be rotated nearly parallel to the incoming light, which is necessary for materials of high refractive index.

5. Align the sample as follows:

(a) Adjust the sample vertically so that it is roughly perpendicular to the horizontal plane.

(b) Using the naked eye, determine whether illuminated spot on the sample remains stationary as the sample is turned. If not, then adjust the goniometer head radially until it does. (Ideally, the centre of rotation of the sample should correspond to the point of intersection of the light source with the polished surface of the sample).

(c) Adjust the sample vertically and horizontally by means of the screws on the goniometer head until the light is reflected from the desired area of the sample.

(d) While viewing through the telescope the light signal reflected from the sample, rotate the sample in the vertical plane by means of the screws on the goniometer head until the signal is precisely parallel to the vertical cross hair in the telescope.

6. Turn the telescope to a position corresponding to an angle of deviation of about 50°, or the estimated angle of deviation at Brewster's angle. Turn the sample, by means of the goniometer arm, until the signal is approximately centred in the telescope, close the light-proof box, close the slit at the input aperture of the monochromator, darken the room, and mount the photomultiplier tube onto the telescope. (Be sure the high tension is off). When the tube is mounted, turn on the high tension.

7. Carefully open the slit at the input aperture of the monochromator until the signal current is approximately 30 X 10^{-10} amps (30% of full scale). Rotate the telescope arm using the fine adjustment screw until the signal current is approximately at its maximum. Reduce to 30 X 10^{-10} amps using the monochromator input slit. Find Brewster's angle approximately, as follows:

(a) Rotate the telescope arm using the fine adjustment screw and note carefully the maximum signal current.

(b) Turn the crystal a few degrees and rotate the telescope in the same direction until a maximum signal current is again reached or the needle goes off scale.

(c) If the second maximum signal current is greater than the first, the sample has been turned in the wrong direction. Return to instruction 7 (a) and turn the sample in the other direction. If the signal becomes too dim to measure, the intensity can be increased by opening the input slit on the monochromator.

(d) At each setting of the sample, slowly turn the telescope, using the fine adjustment screw, until the maximum intensity reading is reached.

At this point it is necessary to define what is meant by the "maximum intensity". For a given crystal position, as the telescope and photomultiplier tube are rotated into the beam of the reflected light, the signal current varies in a complicated way with the angle of the telescope.

One typical curve is shown in Figure 2, although the pattern may vary from time to time.

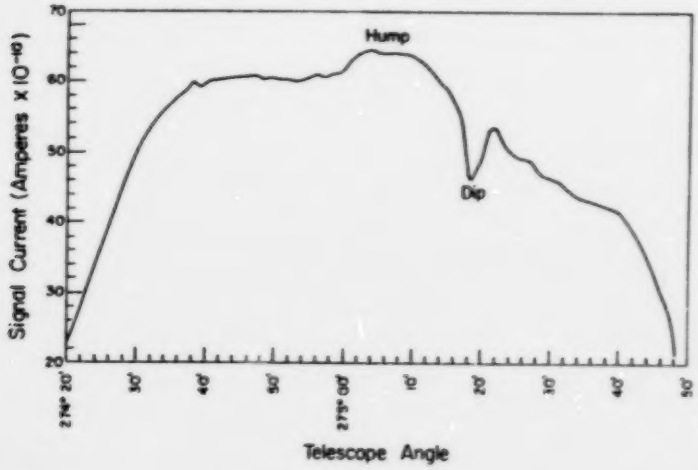

Figure 2 - A typical curve of photomultiplier signal current plotted against telescope angle for a fixed crystal setting.

The example shown has only one true maximum (275 ° 05'), although there may often be a second one at the lower angle reading (about 274 ° 50') which may be higher in value than the former. A prominent feature of the curve is the "dip" at 275 ° 18 1/2' which is caused by the signal being obscured by the cross hairs in the telescope. In actual measurement, this shows as a sudden swing of the ammeter needle to the left and back again, and can be distinguished from normal "noise" fluctuations only by its magnitude.

However, by careful use of the fine adjustment, the telescope can be adjusted so the signal current will correspond to the bottom of the dip. When this is done, the signal is centred on the cross hairs, at least as far as the photomultiplier is concerned. The angle of deviation of the light beam can then be read quite accurately. This angle will not correspond exactly to the angle that would be obtained if the signal were centred on the cross hairs visually but this discrepency, usually amounting to only a few minutes of arc, is allowed for in the final results.

The light intensity reading for a given angle is usually considered as being the top of the hump closest to the dip. In the example shown, this would correspond to 64 1/2 in the vicinity of 275 ' 05'. It is best measured by slowly moving the telescope by means of the fine adjustment screw, turning at about 1/10 turn per second. This is fast enough to eliminate minor fluctuations and slow enough to catch the maximum. This speed should be changed to suit the ammeter used.

It may happen, since the pattern may change form, that the dip neatly splits the hump, giving two peaks. In this case, either peak is selected, and the same one used throughout the experiment. It has been found that the pattern is fixed once the photomultiplier tube is in place on the telescope and the dip does not change its relative position on the curve, regardless of the sample setting.

The only real requirement for a reading is that the same point on the pattern should be used for each measurement in an experiment so that all readings are comparable. Brewster's angle is approximated by the setting that gave the lowest light intensity reading.

8. Adjust the input monochromator slit until the signal current is about 83 X 10^{-10} amps. If the input slit needs to be opened to more than 2.00 mm, it is advisable that the output slit be opened more, as well, but not beyond 0.30 mm. On the other hand, if the input slit can be closed to less than 0.35 mm, it may help if the output slit is closed somewhat, but only if care has been taken in making the signal parallel to the vertical cross hair in the telescope.

Note: Before taking the following readings, ensure that the photomultiplier tube has been turned on for at least thirty minutes.

9. Rotate the sample away from the approximate Brewster angle setting until a reading of about 95 X 10^{-10} amps is obtained. (This means a rotation of about 1 1/2° for sphalerite, but it depends on the mineral and the wavelength). The sample may be rotated in either direction but, because of the mechanical features of the apparatus being used, a counterclockwise rotation, when viewed looking downward, is preferable.

10. With as many lights out as possible (with the enclosure closed, a background light equivalent to a reading of less than 15 X 10^{-10} amps is obtained when all the overhead lights are on) take a light intensity reading as defined under 7 (d) and record it.

11. Centre the signal current on a dip (see 7 (d)) and read the angular setting of the telescope through the hole in the enclosure, using the battery-powered bulb (switch is on the battery) and a magnifying glass. The magnifying glass may be moved sideways using the two holes in the enclosure on either side of the telescope.

12. Close up the enclosure and turn off the battery-powered light.

13. Rotate the sample about 5 to 10 minutes of arc (1/6 turn of fine adjustment screw for goniometer arm) in the direction opposed to that of 9. It is preferable that no two consecutive light-intensity readings differ by more than 3 X 10^{-10} amps. Then measure the light intensity and telescope position as in paragraphs 8, 10 and 11.

14. Repeat the procedure 10 to 13 until the region of minimum itensity has been passed and the readings are back to about 95 X 10^{-10} amps.

N.B. It is often wise to plot a graph of angle readings versus light intensity readings as they are recorded. The final results depend on the smoothness and completeness of this graph and it is impossible to "go back for more points" after a series of readings nas been taken. It is also recommended that, toward the end of an experiment, readings be taken at some of the earlier settings to see if they can be duplicated. A difference of 1 X 10^{-10} to 2 X 10^{-10} amps may occur; anything greater than this suggests that all the readings should be repeated.

15. When it is felt that sufficient readings have been taken to ensure a suitable curve of angle versus intensity, turn the sample back to approximately the Brewster's angle position and centre the signal current on the dip. Read the telescope setting and record it as under 11 above. With the room darkened and the photo-multiplier tube turned off, remove it from the telescope and cap it. If another experiment is to follow, turn the tube on again to keep it warmed up. Centre the signal on the cross hair visually and read and record the angle of the telescope. The intensity of the signal may have to be increased by opening the monochromator input slit or by turning the wavelength to 5300 A, whichever is easier to see. This gives a relation between the measured angles and the actual angles. A difference of more than plus ten minutes

or less than minus five minutes indicates a probable error.

16. Move the sample radially away from the light source by rotating the goniometer arm to a position perpendicular to the collimator (to give the telescope sufficient room). Move the telescope into direct line with the collimator and centre the signal cross hair. Record the angle. This is the zero position.

17. Plot a graph of angular readings versus light intensity readings, as shown in Figure 3. A skewed, hyperbolic shaped curve should be obtained. The minimum is found by drawing a series of lines through the graph parallel to the abscissa. Find the centre of each line segment as cut off by the graph.

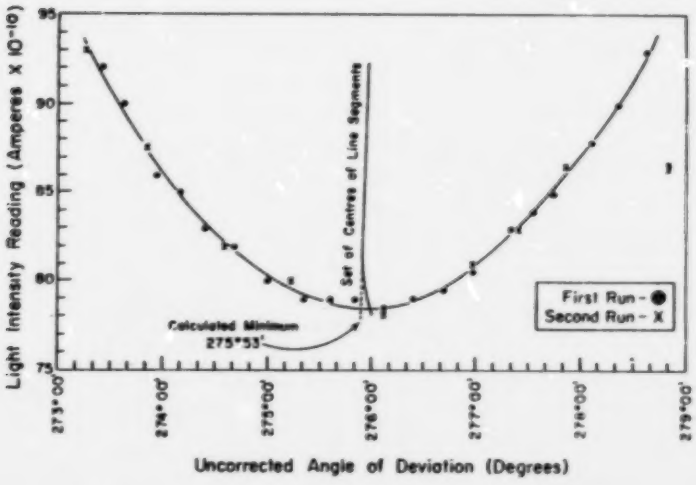

Figure 3 - Intensity of reflected light versus crystal setting for the Timmins sphalerite (λ = 4500 A)

The set of line segment centres forms a line that passes precisely through the bottom of the curve. Any sudden curve in this line toward the bottom of the graph should be ignored as it probably indicates a slight error in drawing the graph. The graphs are almost universally skew and hence the centre line is seldom exactly vertical.

Also, since only a small part of the full curve is used, the centre line seldom differs appreciably from a straight line.

18. Take the angle giving the minimum reading as found above, add the correction due to the photomultiplier tube not entering the signal exactly on the cross hairs, and subtract the zero reading. The result is the angle of deviation (D) at Brewster's angle for which $\beta = 90 - D/2$.

GENERAL INSTRUCTIONS

(a) Handle the photomultiplier with care and do not expose it to a stronger light intensity than exists in a darkened room.

(b) The voltage stabilizer works best when heavily loaded.

(c) As high a resistance as possible should be kept across the ends of the output signal wires of the photomultiplier to avoid overloading the tube. This means that the millimicroammeter should not be turned up from its most sensitive scale even if the needle goes off scale for a time.

(d) Often a transparent crystal will produce more than one reflection, only one of which is from the front surface. The proper signal is sharper than any others and will produce a dip which the others, due to their diffuseness, will not.

(e) The cross hairs may be focused by moving the eye-piece. The focus of the telescope is changed by turning the ring between the aluminum collars.

(f) DON'T JAR THE TABLE. This may change the zero reading. In general, all vibrations should be avoided.

(g) It may happen, on occasion, that the photomultiplier will give violent and extraordinarily high signal currents for no apparent reason. This seems to be caused by light leaks, and disappears after the aluminum casing is re-taped with black plastic electrician's tape.

ACCURACY

The accuracy of the results depends almost wholly on the accuracy of the curve of angle versus intensity. The intensity varies considerably with angle except in the immediate vicinity of Brewster's angle. As a consequence, the sides of the graph can be drawn more accurately than the bottom. This is made use of in the method described for finding the minimum. The sharpness of the curve, i.e. the rate of change of slope at Brewster's angle, appears to increase with increasing wave length of the light. This is probably due to the greater effectiveness of the Polaroid in the red part of the spectrum.

There is a certain amount of noise in the signal current of the photomultiplier, which limits the sensitivity of the light intensity readings. This noise seldom amounts to more than 1×10^{-10} amps and is believed to be due to electrical interference. This noise may increase due to mechanical vibrations or failure of the electrical system (in particular, a light source

that is on the verge of burning out). Usually the noise, which makes itself manifest as sudden deviations from a central position, may be distinguished from the signal by observing the movements of the needle for a few seconds. The noise may be reduced by connecting a capacitance across the signal wires but if too much damping is introduced, it may be impossible to find the dip in the signal pattern.

In general, the accuracy depends on the curve of intensity versus angle, which, in turn, depends mainly on the precision with which the light intensity is measured. Every means possible should be taken to ensure stability over both a long and short periods of time. With the equipment as it exists, the intensity can be measured with an uncertainity of $\pm$ 1/2% on some days and $\pm$ 2% on others. On the average, $\pm$ 1% uncertainty can be expected, which allows measurement of Brewster's angle for sphalerite to an uncertainty of $\pm$ 5' at the red, to $\pm$ 20' at the blue end of the spectrum. No hard-and-fast rule can be made, however, and the degree of accuracy is subjective.

APPLICATION OF THE METHOD TO MINERAL SAMPLES

The apparatus was used, as described above, to measure Brewster's angle for garnet, fluorite, sphalerite, pyrite and iron, and thereby to determine their refractive indexes. All minerals except iron gave well-defined curves of intensity versus angle, although pyrite showed the least polarizing effect and fluorite the most. There was no detectable variation of intensity with

angle for iron between 4000 and 6000 A. The refractive index of fluorite at 5500 A, obtained from the Brewster's angle relationship, is 1.433 $\pm$ 0.005, which is in extremely good agreement with the textbook value of 1.434. The refractive index of the garnet sample at 5500 A, determined by this method, is 1.793 $\pm$ 0.007 which, again, is in good agreement with the value of 1.800 measured by oil immersion methods.

The Brewster's angle for pyrite gave a refractive index of 4.06 at 6000 A. An incomplete experiment conducted at 4000 A indicates a substantially lower refractive index at that wavelength.

The Brewster's angles for both the garnet and a number of sphalerite samples were measured at a number of wavelengths between 4000 A and 6000 A. The results are shown in Figures 4 and 5.

The refractive indexes of the Santander and Sonora sphalerites are substantially lower than those reported in the literature, which are shown in Figure 5 as the curve marked "Index of Refraction of Z_nS", although chemical analyses of these samples indicated a high degree of purity. The sphalerite from Timmins and Chihuahua, both of which contain major amounts of iron, gave higher values than the Santander and Sonora samples.

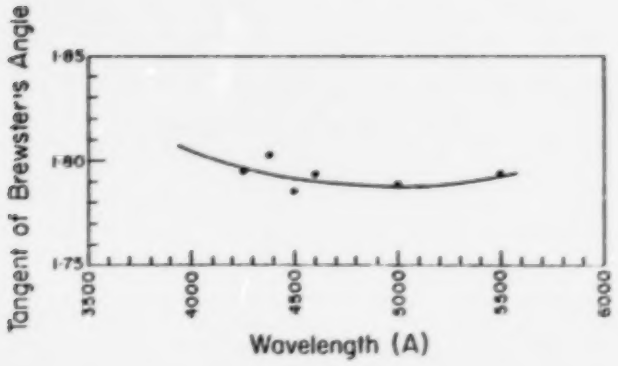

Figure 4 - Variation of the tangent of Brewster's angle of garnet with wavelength of light employed.

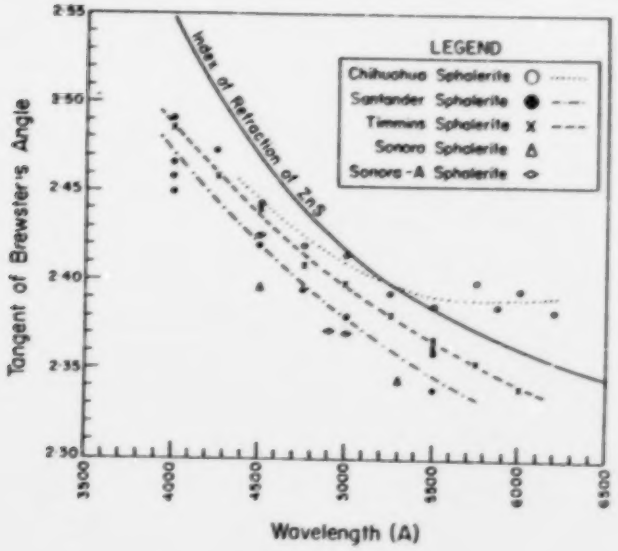

Figure 5 - Variation of the tangent of Brewster's angle of various sphalerites with wavelength of light employed.

CONCLUSIONS

The apparatus and procedure as outlined above is capable, under normal conditions, of measuring Brewster's angle to a small fraction of a degree (the tangent, accurate to one or two in the second decimal place). The accuracy is limited by the rate of change of slope of the curve of intensity versus angle at its minimum. It should be possible to make this sharper by use of a finer Polaroid and a better collimated beam of light (using a slit of less height). This, in conjunction with a more stable mechanical and electrical system, might enable measurements accurate to one minute to be made. However, a stronger light source would also be needed for a more sensitive photomultiplier, and the optical system would have to be carefully gone over. A point that should be carefully checked, for example, is whether the incident and reflected beams lie in a plane parallel to the plane of rotation of the telescope.

Thus it appears that Brewster's angle can be measured with quite good precision if adequate equipment is provided.

ACKNOWLEDGEMENTS

The writer wishes to acknowledge the assistance provided by S.A. Forman and E.H. Nickel of the Mineralogy Section, by J.F. Rowland of the Physical Chemistry Section, and by various personnel in the Mineral Physics Section.

JDB:cc

ADDENDUM

On August 31, 1965, Prof. G. Lansraux of the Division of Applied Physics of the National Research Council in Ottawa kindly consented to come to the Mines Branch to discuss possible reasons for the discrepancy between the actual refractive index of sphalerite and the values obtained by the method of Brewster's angle. Also present at this meeting were J. Butterill, J.D. Keys, S.A. Forman, J.F. Rowland and E.H. Nickel.

Prof. Lansraux suggested that the following modifications should be made to the optical system:

(a) The slit limiting the size of the light beam emerging from the monochromator should be widened and shortened.

(b) The pinhole device between the goniometer collimator and the sample should be removed.

(c) The Polaroid film should be placed in the reflected beam rather than the incident beam. This can be done by attaching it to the viewing telescope.

Prof. Lansraux felt that this would improve the operating conditions, although it might still not remove the sphalerite discrepancy. He suggested, further, that surface effects caused by the polishing procedure might provide an explanation. Another possibility that arose during the discussion is that the existence of a thin oxide film on the sphalerite surface might have an effect on the determination, since the determination of Brewster's angle

is a surface method. This possibility derives support from the fact that zinc oxide has an appreciably lower refractive index than does zinc sulphide.

Continuation of the investigation of this method is planned.

E. H. Nickel,
Head,
Mineralogy Section